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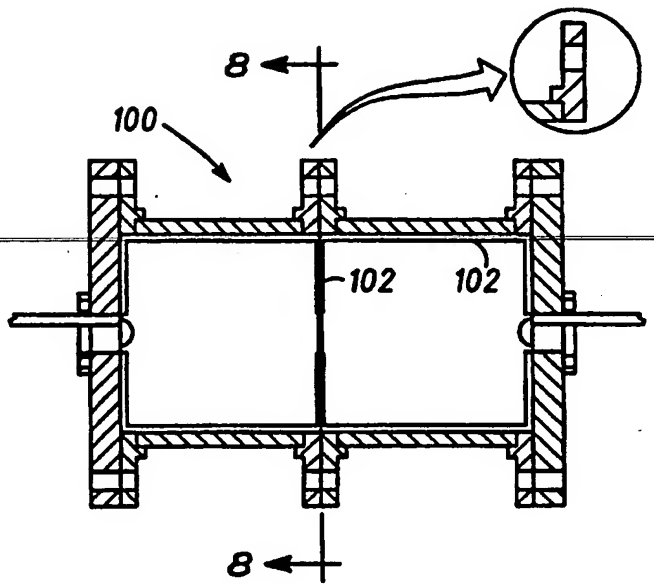
(54) Title: METHOD FOR PRODUCING HIGHLY TEXTURED YTTRIUM BARIUM CUPRATE FOR USE IN WAVEGUIDES AND TRANSMISSION LINES

(57) Abstract

A method of preparing an article of manufacture of a superconductive waveguide (100) and transmission line (104). The method includes preparing a mixture of superconductive material constituents, disposing the constituents on a silver containing substrate in the desired shape of the waveguide (100), heating the mixture of constituents on the silver containing substrate, heating the mixture in a first atmosphere having a partial pressure of CO_2 to control decomposition of at least one of the superconductor material constituents and changing the first atmosphere to a second atmosphere consisting essentially of an oxidizing gas capable of allowing decomposition of at least one of the superconductor material constituents. The reactive texture process can be used to dispose superconducting material on selected components of waveguides (100) and transmission lines (104).



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Method for Producing Highly Textured Yttrium Barium Cuprate for Use in Waveguides and Transmission Lines

Background of the Invention

This invention was developed in part under U.S. Air Force Contract F19628-91-C-0082, and the U.S. government has certain rights in this invention pursuant to this contract.

The present invention relates generally to high temperature superconductor material structures useful in waveguides and transmission lines. More particularly, the invention relates to waveguides and transmission lines including reactive textured, high temperature superconductor ceramic ("HTSC") materials and methods of use of such waveguides and transmission lines.

High temperature superconducting ceramics (HTSC) are intrinsically weak and brittle materials. In addition, conventional ceramic processing of these materials produces polycrystalline bodies which have low critical current densities (j_c, in DC measurements) and high surface resistivities (R_S, in RF measurements). Commercial applications of these materials require components that exhibit high j_c and/or low R_S values, as well as the capability of producing mechanically strong and easy to manufacture components. Due to the materials' low mechanical strength, commercially useful structures such as waveguides and transmission lines cannot be produced without the use of a substrate to impart strength and toughness to the superconductor. This is especially true for lower frequency RF devices that require the superconductor to be formed into relatively large, complex shapes. HTSC thin films, for example, (less than about 1 micron thickness) have been shown to have high current densities and low R_S values. However, these films are not useful for low frequency RF applications because they require expensive single crystal substrates (typically, $LaAlO_4$ or $SrTiO_4$) and can only be formed into planar structures with dimensions under a few inches.

Bulk HTSC materials with highly textured microstructures can exhibit the level of electrical performance required for commercial waveguide applications. For $YBa_2Cu_3O_{7-x}$, such textured microstructures are produced using a method called peritectic re crystallization

or, more commonly, "melt-texturing". In this process, "textured" $YBa_2Cu_3O_{7-x}$ is produced by crystallizing this compound out of its peritectic mixture of Y_2BaCuO_5 plus a Ba/Cu-rich liquid. Many variations of this technique have been described, and it is commonly practiced in laboratories throughout the world. However, the process remains essentially the same as that originally developed in 1988.

The melt-texturing process typically involves heating a sample above the peritectic temperature (1015°C in air) to decompose the $YBa_2Cu_3O_{7-x}$ into Y_2BaCuO_5 plus liquid. This mixture is cooled slowly through the peritectic temperature allowing $YBa_2Cu_3O_{7-x}$ to crystallize. When this cooling is performed in the presence of a thermal gradient, the $YBa_2Cu_3O_{7-x}$ grains preferentially grow parallel to the gradient and a "textured" microstructure results. The slow cooling keeps the nucleation rate of $YBa_2Cu_3O_{7-x}$ low, resulting in the formation of a small number of nuclei. As a result, the $YBa_2Cu_3O_{7-x}$ grains can grow to very large sizes before impingement; and if the cooling is performed in a thermal gradient, the grains will be highly aligned. In the originally developed process, samples were determined to have critical currents of up to 17,000 A/cm^2 in self-field with only a small magnetic field dependence. Improvements to this process (which have included the production of continuous lengths of melt-textured filaments) have resulted in measured current densities as high as 140,000 A/cm^2 in self field and 44,000 A/cm^2 in a 1 Tesla field at 77 K.

While the melt-texturing process has proven to be very effective in the fabrication of bulk $YBa_2Cu_3O_{7-x}$ having properties approaching those of thin film materials, it has substantial drawbacks. First, melt-texturing is essentially a crystal growth process in which the rate of material production is controlled by the velocity of the crystallization front. In the case of $YBa_2Cu_3O_{7-x}$ crystallizing out of its peritectic mixture, the crystallization rate is extremely sluggish. Even in extremely large thermal gradients (10^7 K°/m) growth rates of only 1.2 cm/hr have been achieved. A second problem, of particular importance to texturing thick film structures, is the fact that the melt-texturing process requires processing at temperatures above 1000°C in the presence of the extremely reactive peritectic liquid. This severely limits the choice of substrate materials that can be used without reacting with the superconductor to form

undesirable layers between the substrate and superconductor. To date, only zirconia and magnesia have been used with any degree of success, and these ceramics are expensive and difficult to process.

It is therefore an object of the invention to provide an improved method of producing a waveguide using high temperature superconductor (HTSC) material.

It is a further object of the invention to provide a novel method of producing an HTSC material-containing waveguide at relatively low temperatures with very high rate of production.

It is another object of the invention to provide an improved method of producing waveguides including HTSC structures on relatively inexpensive substrates.

It is yet a further object of the invention to provide a novel HTSC power transmission line and an improved method of use of same.

It is still another object of the invention to provide an improved waveguide with high Q values arising from an HTSC thick film coated portion.

Further objects and advantages of the present invention, together with the organization and manner of operation thereof, will become apparent from the following detailed description of the invention when taken in conjunction with the accompanying drawings, wherein like elements have like numerals throughout the drawings.

Brief Description of the Drawings

FIG. 1 illustrates a 40X magnification microstructure of reactively textured $YBa_2Cu_3O_{7-X}$ on silver buffered stainless steel;

FIG. 2 shows a reactively textured $YBa_2Cu_3O_{7-x}$ on a silver substrate at 40X magnification;

FIG. 3 illustrates a conventional peritectic re crystallized thick film microstructure on a zirconia substrate;

FIG. 4A illustrates an exemplary rocking angle X-ray diffraction curve showing the highly textured nature of an HTSC material prepared by one of the methods of the invention; and FIG. 4B shows X-ray diffraction patterns for three crystalline $YBa_2Cu_3O_{7-x}$ samples;

FIG. 5 illustrates a pseudobinary phase diagram of Y_2BaCuO_2 and 3BaO·5CuO;

FIG. 6 shows surface RF resistivity extrapolated to 1GHz for $YBa_2Cu_3O_{7-x}$ specimens of the invention, a prior art sintered $YBa_2Cu_3O_{7-x}$ and Cu;

FIG. 7 illustrates a side view of a waveguide constructed in accordance with one form of the invention;

FIG. 8 shows a front sectional view taken along lines 8-8 of the waveguide illustrated in FIG. 7;

FIG. 9A illustrates resonator Q versus surface resistance for a copper cylinder compared to a YBCO cylinder, each with a YBCO center conductor; FIG. 9B illustrates an unloaded resonator Q versus outer radius of a coaxial resonator with a copper outer wall and YBCO center conductor; FIG. 9C illustrates unloaded Q values at 77°K versus dissipated power for a 1.5 inch diameter, 6 inch long halfwave coaxial resonator with 0.25 inch diameter HTSC center conductor fabricated by depositing a reactively textured YBCO thick film onto a stainless steel substrate.

FIG. 10 illustrates a high power coaxial transmission line having a high temperature YBCO superconductor thick film on a center conductor; and

FIG. 11 illustrates power dissipation versus input power for a copper center conductor compared to a YBCO center conductor power transmission line at 77°K and 1 GHz frequency.

Detailed Description of Preferred Embodiments

A process of producing a waveguide in accordance with one form of the invention involves the crystallization of $YBa_2Cu_3O_{7-x}$ out of a metastable liquid formed by rapidly introducing a non-equilibrium mixture of Y-, Ba-and Cu-compounds (mixed in the appropriate stoichiometry) into a combination of temperature and a gas atmosphere in which $YBa_2Cu_3O_{7-x}$ is the thermodynamically stable phase (hereinafter generally referred to as "reactive texturing process"). Two general variations of this process have been successfully demonstrated. In the first general method of preparation, Y_2O_3, CuO, and $BaCO_3$ powders are mixed in a molar ratio of 0.5:3.0:2.0 and are heated in a CO_2-rich atmosphere to approximately 850°C to 890°C. The atmosphere is then changed to 2 torr of pure oxygen. The use of a

CO_2-rich atmosphere during heating suppresses the decomposition of $BaCO_3$ and consequently prevents $YBa_2Cu_3O_{7-x}$ from forming prematurely. When the atmosphere is rapidly changed to a reduced pressure oxygen environment, the reaction mixture begins to decompose to a partially molten state out of which $YBa_2Cu_3O_{7-x}$ crystallizes.

In a second general method of preparation, a prereacted, phase-pure $YBa_2Cu_3O_{7-x}$ powder is heated to approximately 850°C to 890°C, also in a CO_2-rich atmosphere. Without limiting the scope of the invention, it is believed the presence of the CO_2 causes the $YBa_2Cu_3O_{7-x}$ to decompose into a complex mixture of oxides and oxycarbonates. As for the first general method, the atmosphere is changed at temperature to a reduced pressure oxygen containing atmosphere, which causes this mixture to decompose into the partially molten state from which $YBa_2Cu_3O_{7-x}$ can crystallize.

In accordance with one form of the invention, this reactive texturing process is preferably carried out on either a silver foil or a base metal, such as a stainless steel, which has been electroplated with either silver or silver with a nickel intermediate layer. In this embodiment the silver or silver/nickel buffer layers are necessary since $YBa_2Cu_3O_{7-x}$ and its precursors are relatively active compounds which react strongly with most base metals. However, silver is relatively inert with respect to $YBa_2Cu_3O_{7-x}$. This silver or silver/nickel buffer layer is preferably at least 0.002" thick to protect the superconductor. Base metals which have proven satisfactory include, for example, stainless steels, such as 302 stainless steel, 304 stainless steel, 316 stainless steel and also Inconel 600. The process has been practiced on a variety of shapes, including discs, tubes, wires and coils. Copper can also be used in the low temperature range of the reactive texturing process. However, the successful use of copper as a substrate requires use of an appropriate intermediate metal which will prevent interdiffusion of copper, silver and oxygen.

The substrate can be coated with the precursor slurry of appropriate stoichiometry using either painting, dipping, spraying, or any other technique currently used to apply thick film coatings or patterns. It has been determined that the preferred thickness of this applied coating is about 0.002" to 0.008". The preferred thermal processing has three steps:

1. Binder/organic removal. Heating of the coating is preferably carried out in a reduced total pressure oxygen environment (e.g., 2 torr of oxygen) heated at a rate of between 30°C/hr and 300°C/hr from room temperature to a temperature between 350°C and 500°C which is sufficient to removal the volatile components of the precursor paint.

2. Reaction suppression/precursor formation. Heating of the coating is preferably performed at a rate of about 300°C/hr. in a nitrogen atmosphere containing between at least about 0.8% and 2.8% CO_2. One can use higher pressures of CO_2, but such higher pressures are more than needed to suppress the decomposition of $BaCO_3$ or initiate the decomposition of $YBa_2Cu_3O_{7-x}$. The CO_2 can be mixed with any inert gas, such as N_2, argon or helium. The temperature is preferably between the temperature of the binder removal stage and the temperature of the crystallization stage. These temperatures are sufficient to suppress the formation of $YBa_2Cu_3O_{7-x}$ in the case of an oxide/carbonate precursor or decompose the $YBa_2Cu_3O_{7-x}$ precursor to an appropriate mixture of oxides and oxycarbonates.

3. Crystallization. A preferred window for crystallization of $YBa_2Cu_3O_{7-x}$ exists between about 850°C and 900°C in an atmosphere of about 1 to 3 torr of oxygen, although the oxygen pressure can range up to one atmosphere pressure. Below about 850°C, the grain sizes are greatly reduced in size. It should also be noted that at higher oxygen partial pressures, the process temperature increases such that at 0.21 atm. oxygen the temperature of treatment would be about 975°C. Preferably the process temperature is maintained below the melting point of the silver containing substrate. Most preferably, therefore, the pressure of oxygen is kept below about 50 torr to operate at a temperature below 925°C (the melting point of silver at 50 torr). One can choose to perform the process by slowly increasing the temperature within this window during the crystallization process as opposed to using a simple isothermal hold. Either procedure is acceptable.

In the above described preferred process an intermediate product, or article of manufacture, is obtained. In the conventional melt texturing process the peritectic zone (region P in FIG. 5) encompasses the region of the phase diagram involved in producing the desired $YBa_2Cu_3O_{7-x}$. In this conventional method the amount of liquid present is quite large

throughout the processing temperature range (about 1015°C then cooled slowly through the peritectic temperature of 1013°C). On the other hand in the instant invention, rather than having an intermediate product of solid material and a substantial percentage of peritectic liquid, the intermediate product is primarily a solid and a small fraction of a eutectic liquid (not a peritectic liquid). Since the reactants are metastable, the liquid that forms is the lowest melting liquid in the Y-Ba-Cu-O system, that is, the ternary eutectic. Substantial advantages result from being able to prepare textured $YBa_2Cu_3O_{7-x}$ without excess liquid present. One such advantage is the ability to cast well defined solid patterns without need of liquid barriers in place. A desired pattern can be disposed on a substrate, such as by applying a thick film slurry in a desired pattern; and then the $YBa_2Cu_3O_{7-x}$ can be formed by the method of the invention without substantial liquid flowage causing loss of the shape of the desired pattern. Thus, the intermediate product of the invention formed at about 850-900°C does not have the undesirable large liquid component present in the conventional intermediate product formed in the peritectic region.

A process has been described herein which produces textured $YBa_2Cu_3O_{7-x}$ microstructures, as in the peritectic re crystallization method. However, unlike peritectic re crystallization, the instant method produces these microstructures at low temperatures (less than about 900°C) and in relatively short times (less than about 1 hr compared to 10-15 hours for conventional melt texturing). This combination of low temperatures and short times enables the use of relatively inexpensive and easy to form base metal substrates that substantially reduce the potential cost of the component. This cost reduction makes this process much more attractive for the commercial application of HTSC components. This process is especially attractive for the fabrication of three dimensional RF resonant structures which are the fundamental components of numerous RF devices such as filters, oscillators, combiners and radar units. As can be seen in FIG. 6, the resulting $YBa_2Cu_3O_{7-x}$ exhibits a substantially improved RF resistivity over both conventional copper and over a prior art $YBa_2Cu_3O_{7-x}$ prepared by sintering and disposed on a silver substrate.

In another aspect of the invention FIG. 7 illustrates a side elevation view of a waveguide 100 constructed in accordance with the invention. The waveguide 100 is a two pole filter assembly having reactively textured thick film 102 of YBCO disposed on the inner walls of the waveguide 100. FIG. 8 illustrates a cross sectional view of the waveguide 100. Further details of waveguide construction and other embodiments are set forth in a co-pending application 08/349,060, which is incorporated by reference here. The calculated resonator Q versus surface resistance behavior of a waveguide structure is illustrated in FIG. 9A which compares the Q values of a copper outer cylinder with a YBCO high temperature superconductor cylinder, each having a high temperature superconductor coated (or optionally a solid) center resonator ring. These values were obtained by using conventional, well known geometry factor measurements in which the geometrical features were removed, enabling determination of the effect of the YBCO material used, alone, versus the same geometry using copper or other conventional materials.

In another form of the invention, one can calculate Q values using conventional computer software (for example, "Emenance" from AnSoft Corp., Pittsburgh, PA or "EMAS" from McNeil-Schcoenneller Corp., Milwaukee, WI. Such a commercial finite element analysis code (known conventionally as "FEA" code) of AnSoft can be used to simulate various features of RF filters. This type of code is accepted as accurately predicting resonator Q and frequency, given various input parameters, including resonator geometry and electrical conductivity (loss tangent). These types of codes also accurately calculate coupling between two or more adjacent waveguide resonators. The AnSoft computer software code solves the known electromagnetic field equations of the three-dimensional waveguide structure, including performing a known asymptotic waveform evaluation to produce the frequency response of a waveguide. Such conventional computer software code is divided into three parts: (1) a solid modeler section allows the user to input the geometry of the device and input/output couplers using a CAD interface, (2) a finite element solver determines the finite element matrix, and (3) a post processor section allows the user to view the electric and magnetic field patterns at user selected frequencies, as well as the insertion and return losses versus frequency.

As illustrated in FIG. 9A, the geometry factor on toroid measurements for a copper cylinder geometry factor measurement show the typical flat plateau wherein losses are dominated by the presence of metal waveguide walls. FIG. 9B shows the results of a conventional analytic solution for the unloaded behavior of Q for a coaxial resonator versus outer radius of a copper cylinder with YBCO center conductor. FIG. 9C shows direct measurements of copper with a YBCO reactively textured unloaded Q versus dissipated power for a coaxial resonator thick film layer on a stainless steel base. Changing from copper to aluminum or any other metal will only move the plateau in FIGS. 9A or 9B slightly up or down. The utilization of the YBCO walls for the coaxial resonator results in substantial improvement of performance over conventional metal waveguide walls.

In another form of the invention shown in FIG. 10, a superconductor thick film transmission line can be constructed to carry high RF power, such as 50-1000W. The transmission line 104 further includes an outer housing 105 and a superconductor thick film 106 is disposed on a substrate 108. The thick film 106 preferably is a reactive texture process thick film, although other embodiments can comprise thick films prepared by other methods, such as peritectic recrystallization. The reactively textured film 106 preferably is deposited on the substrate 108, such as stainless or silver. A peritectic recrystallized film can be deposited on a substrate 108 of zirconia. With these types of high temperature superconductor thick films deposited on stainless steel or zirconia substrates, the losses in a transmission line can be determined using conventional methodologies. Using known R_S versus surface field data for such resonant structures, one can generate functional behavior of dissipated power versus input power for a coaxial transmission line (see FIG. 11). This transmission line has a 0.125 inch diameter 123 YBCO coated stainless steel center conductor in a 1.68 inch diameter copper outer housing, producing a 50 Ω impedance. The space between the inner and outer conductors was filled with MgO with an epsilon of 9.72 and loss tangent of 3×10^{-6}. The 123YBCO geometry shows a substantial advantage over copper in the power range of at least about 1000W and less. When using ceramic superconductors, the power range is generally limited by the limitations on dissipating heat from a ceramic material.

Semi-continuous lengths of the transmission line 104, shown in FIG. 10, can be produced by a variety of techniques, such as continuous firing of the high temperature superconductor in a commercial off-the-shelf belt furnace. Preferably the superconductor is in the form of fine filaments of 123YBCO formed using a known thermoplastic extrusion technique. The filaments are fed to the furnace from a supply spool. These filaments are carried through the furnace on the belt, are sintered and subsequently collected on a large diameter spool (to accommodate brittleness). This methodology can be adapted to the coaxial transmission line embodiment described herein. In the case of stripline or microstrip design, the YBCO thick film can be deposited using various continuous printing techniques on a continuous ribbon of zirconia which can subsequently be fed onto a belt furnace for firing and then spooled. In the case of the coaxial design, a silver-plated stainless steel wire can be coated with a 123YBCO thick film slurry, dried and then fed into a belt furnace. After firing, the center conductor can be swaged using the copper outer housing 105 and an appropriate dielectric, such as quartz, Teflon (registered trademark of DuPont Corp.), MgO and pressurized nitrogen.

The following are nonlimiting examples of methods of preparing HTSC materials.

Examples

Example 1

A mixture of Y_2O_3, CuO, and $BaCO_3$ was mixed in turn with an acrylic binder, a sorbitan trioleate dispersant, and an n-butanol/xylene solvent to make precursor 'paint'. Other suitable carrier formulations can also be used as understood in the art. This paint was then applied to a silver foil using a paint brush. The resultant dried coating was 0.008" thick. This sample was then placed in a controlled atmosphere furnace, heated in 2 torr of oxygen at 60° C/hr to 350°C to insure adequate removal of the organic components of the paint. The atmosphere of the furnace was then changed to 0.9% CO_2 in nitrogen, and the sample was heated to 900°C at a rate of about 300°C/hr. The atmosphere of the furnace was again changed to 2 torr of oxygen, and the sample was held at temperature for 1 hour. This treatment resulted in a textured, crystallized $YBa_2Cu_3O_{7-x}$ microstructure.

Example 2

A commercial $YBa_2Cu_3O_{7-x}$ powder was mixed with an acrylic binder, a sorbitan trioleate dispersant, and an n-butanol/xylene solvent to make a precursor 'paint'. This paint was applied to a 304 stainless steel disc, a 316 stainless steel disc, and an Inconel 600 disc (all 1.125" diameter and previously electroplated with 0.002" of silver) with a paint brush. The resultant dried coating was, in all cases, about 0.004 to 0.005" thick. All three samples were then placed in a controlled atmosphere furnace, and heated in 2 torr of oxygen at 60°C/hr to 350°C to insure proper removal of the organic components of the paint. The atmosphere of the furnace was then changed to 1.1% CO_2 in nitrogen, and the sample was heated to 880°C at a rate of 300°C/hr. The atmosphere of the furnace was again changed to 2 torr of oxygen, and the furnace temperature was slowly increased at a rate of 25°C/hr to 900°C. This treatment resulted in a textured, crystallized $YBa_2Cu_3O_{7-x}$ microstructure for all samples.

Example 3

A variety of starting materials different from those used in Examples 1 and 2 also proved satisfactory. These starting materials included: (1) phase pure $YBa_2Cu_3O_{7-x}$ with 22% Y_2BaCuO_5, (2) $YBaSrCu_3O_{7-x}$ with 22% Y_2BaCuO_5, (3) a CuO rich commercially available $YBa_2Cu_3O_{7-x}$ and stoichiometric $YBa_2Cu_3O_{7-x}$. All of these starting materials were used successfully in implementing the methods described in Examples 1 and 2.

Example 4

Any one of the above example procedures was followed and the pattern of the original starting material remained substantially the same after preparing $YBa_2Cu_3O_{7-x}$. This was compared to conventionally prepared $YBa_2Cu_3O_{7-x}$ (peritectic processing) which showed substantial liquid flowage and loss of the spatial pattern of the original starting material.

While preferred embodiments of the invention have been illustrated and described, it will be clear to those skilled in the art that various changes and modifications can be made therein without departing from the invention in its broader aspects as set forth in the claims provided hereinafter. Various features of the invention are defined in the following claims.

What Is Claimed Is:

1. A method of producing a waveguide, comprising the steps of:

preparing a mixture of superconductor material constituents;

disposing said constituents on a portion of a waveguide structure;

heating said mixture in a first atmosphere having a partial pressure of CO_2 controlling decomposition of at least one of said superconductor material constituents; and

changing said first atmosphere to a second atmosphere consisting essentially of an oxidizing gas capable of allowing decomposition of at least one of said superconductor material constituents.

2. The method as defined in Claim 1 wherein said portion of the waveguide structure comprises at least one of a center conductor rod and a waveguide housing.

3. The method as defined in Claim 1 wherein said first atmosphere consists essentially of a carbon dioxide-containing gas.

4. The method as defined in Claim 3 wherein said CO_2 containing gas comprises at least about 0.8-2.8% by volume CO_2.

5. The method as defined in Claim 1 wherein said second atmosphere comprises a reduced pressure oxygen gas.

6. The method as defined in Claim 5 wherein said oxygen environment comprises at least about 1-3 torr pressure of oxygen.

7. The method as defined in Claim 1, wherein said superconductor starting constituents comprise at least one of (a) a mixture of Y_2O_3, CuO and $BaCO_3$ (b) phase pure $YBa_2Cu_3O_{7-x}$ with 22% Y_2BaCuO_5, (c) $YBaSrCu_3O_{7-x}$ with 22% Y_2BaCuO_5, (d) CuO rich $YBa_2Cu_3O_{7-x}$ and (e) $YBa_2Cu_3O_{7-x}$ powders.

8. The method as defined in Claim 5 wherein said superconductor starting constituents of group (a) are mixed in a molar ratio of about 0.5:3.0:2.0.

9. The method as defined in Claim 1 wherein said first and second atmosphere include an inert gas.

10. A superconductor material and composite structure, comprising $YBa_2Cu_3O_{7-x}$ disposed on a silver substrate without material interdiffusion therebetween.

11. The superconductor material as defined in Claim 10 wherein said silver substrate is selected from the group consisting of silver and silver coated base metal.

12. A superconductor waveguide, comprising:

A plurality of substantially cylindrical structures coupled together along a longitudinal axis, each of said, cylindrical structures substantially having end walls including apertures located along said longitudinal axis; and a high temperature superconducting material disposed upon interior portions of said substantially cylindrical structures.

13. The superconductor waveguide as defined on Claim 12, wherein said high temperature superconducting material composes $YBa_2Cu_3O_{7-x}$.

14. The superconductor waveguide as defined in Claim 13, wherein, said high temperature superconducting material is prepared from a mixture of superconductor material constituents by heating said mixture in a first atmosphere having a partial pressure of CO_2 controlling decomposition of at least one of said superconductor material constituents; and

changing said first atmosphere to a second atmosphere consisting essentially of an oxidizing gas capable of allowing decomposition of at least one of said superconductor material constituents.

15. The superconductor waveguide as defined in Claim 12, further including two electrical poles coupled to said substantially cylindrical structures.

16. The superconductor waveguide as defined in Claim 12 wherein said waveguide comprises a coaxial transmission line.

17. The superconductor waveguide as defined in Claim 16 where said waveguide includes a coaxial center conductor coated with said high temperature superconducting material.

18. The superconductor waveguide as defined in Claim 17 wherein said superconducting material consists essentially of a reactively textured thick film.

19. The superconductor waveguide as defined in Claim 18 wherein said superconducting material is disposed on a substrate selected from the group consisting of stainless steel, silver and silver-coated base metals.

20. The superconductor waveguide as defined in Claim 17 wherein resonator Q of said waveguide varies in a linear logarithmic manner with surface resistance.

Fig. 1

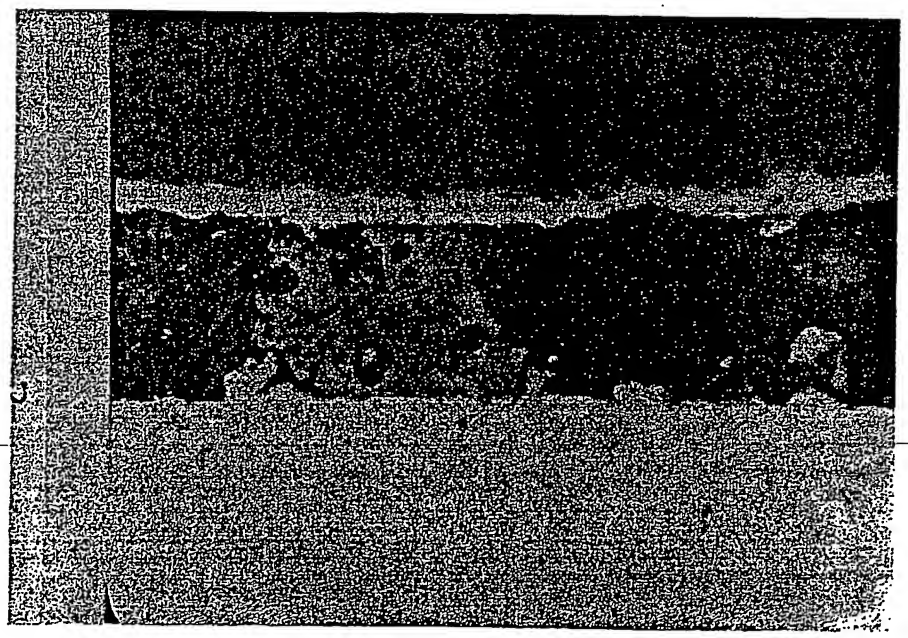


Fig. 2

Fig. 3

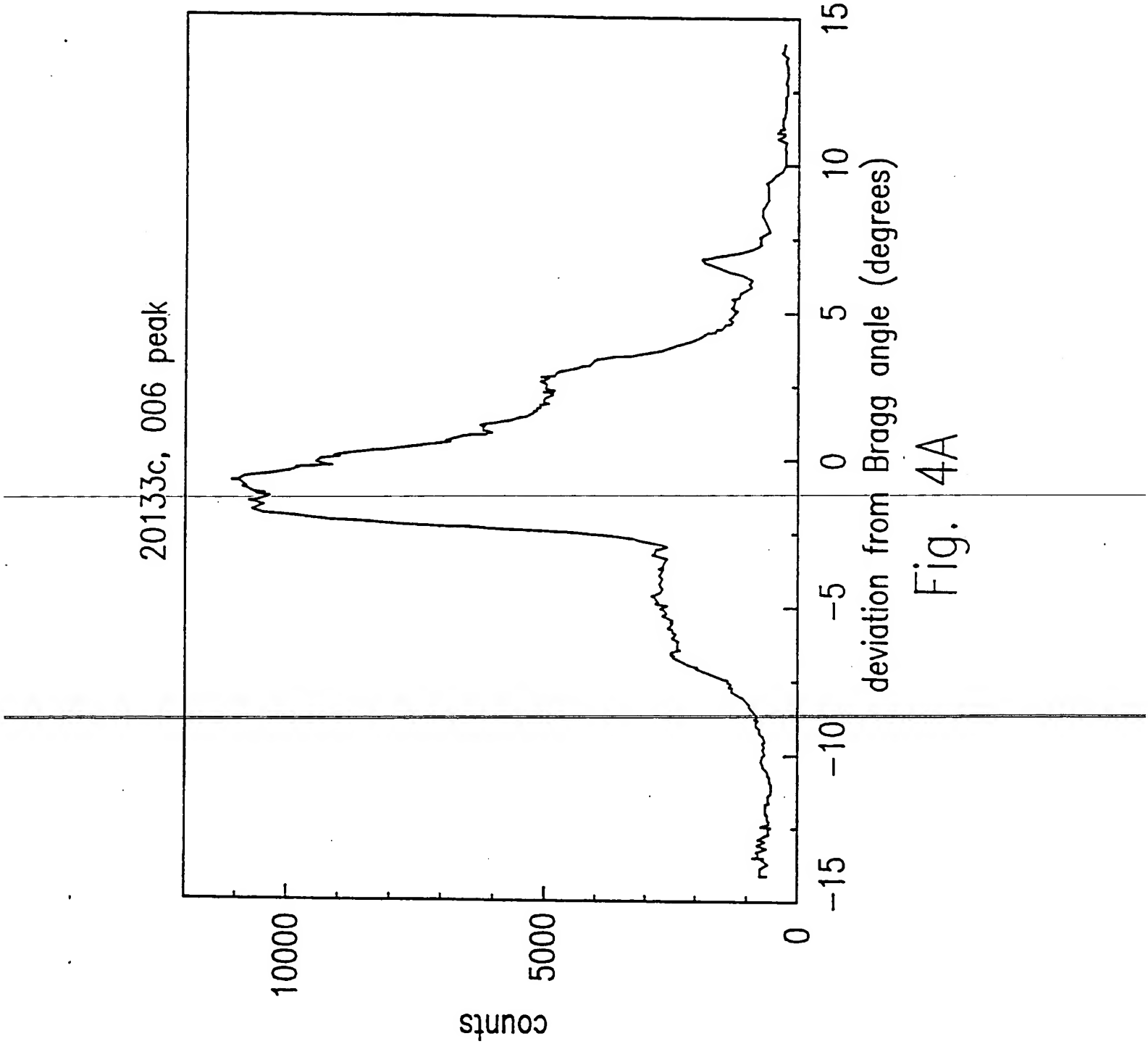

20133c, 006 peak
counts
10000
5000
0
15
10
5
0
−5
−10
−15
deviation from Bragg angle (degrees)

Fig. 4A

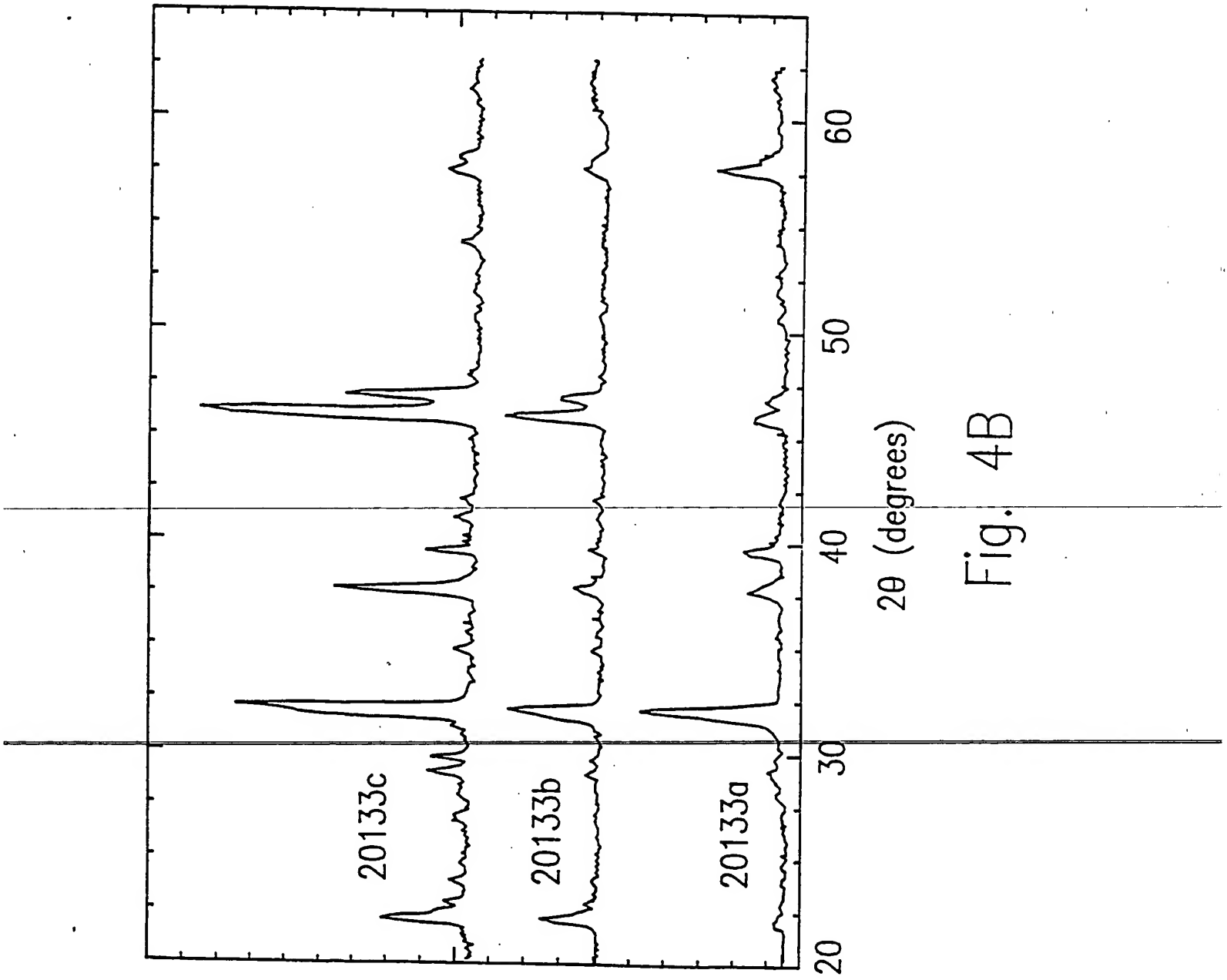


Fig. 4B

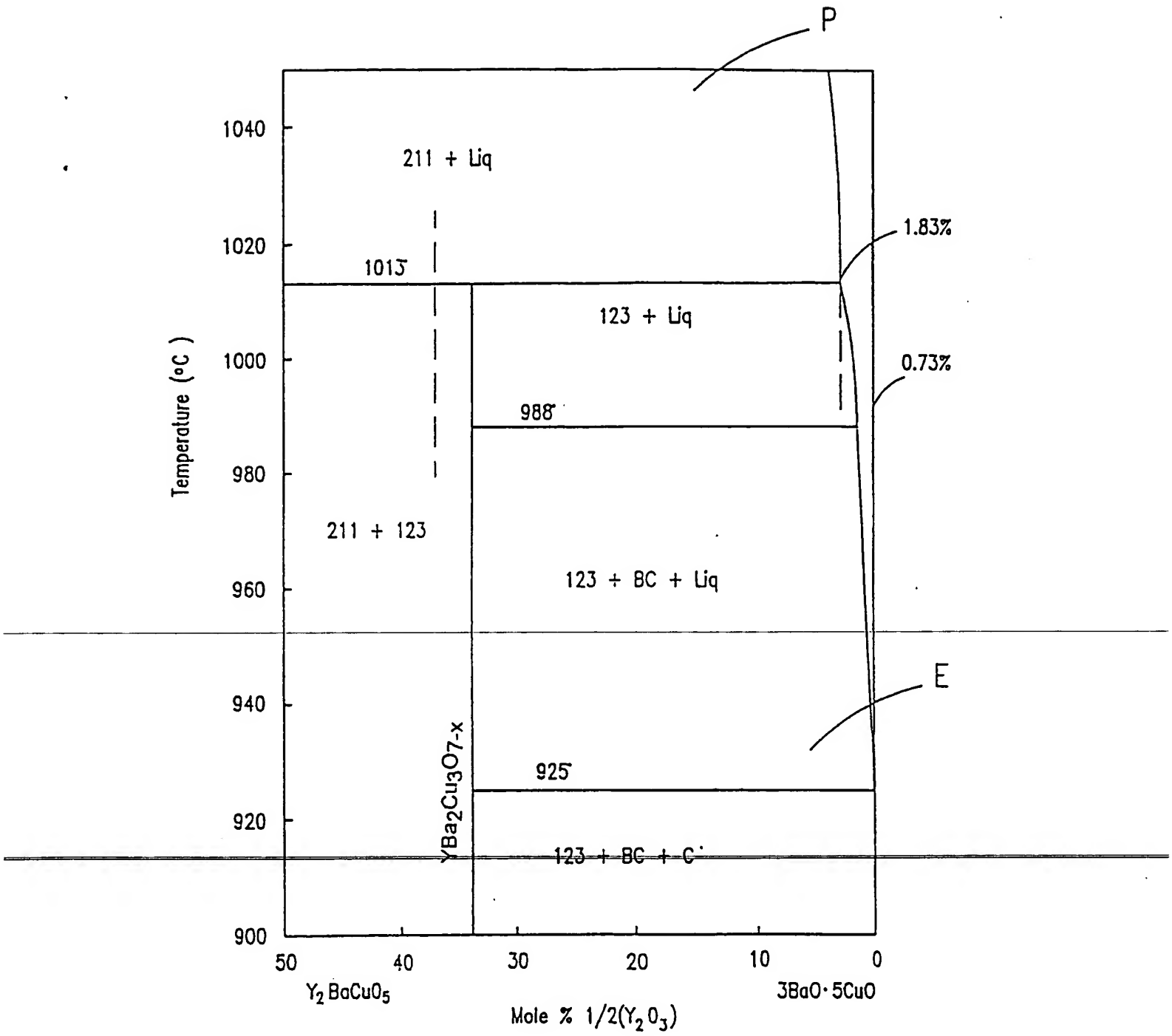

P
1040
211 + Liq
1020
1.83%
1013
123 + Liq
1000
0.73%
988
Temperature (°C)
980
211 + 123
123 + BC + Liq
960
E
940
925
920
YBa2Cu3O7-x
123 + BC + C
900
50
40
30
20
10
0
Y2BaCuO5
3BaO·5CuO
Mole % 1/2(Y2O3)

Fig. 5

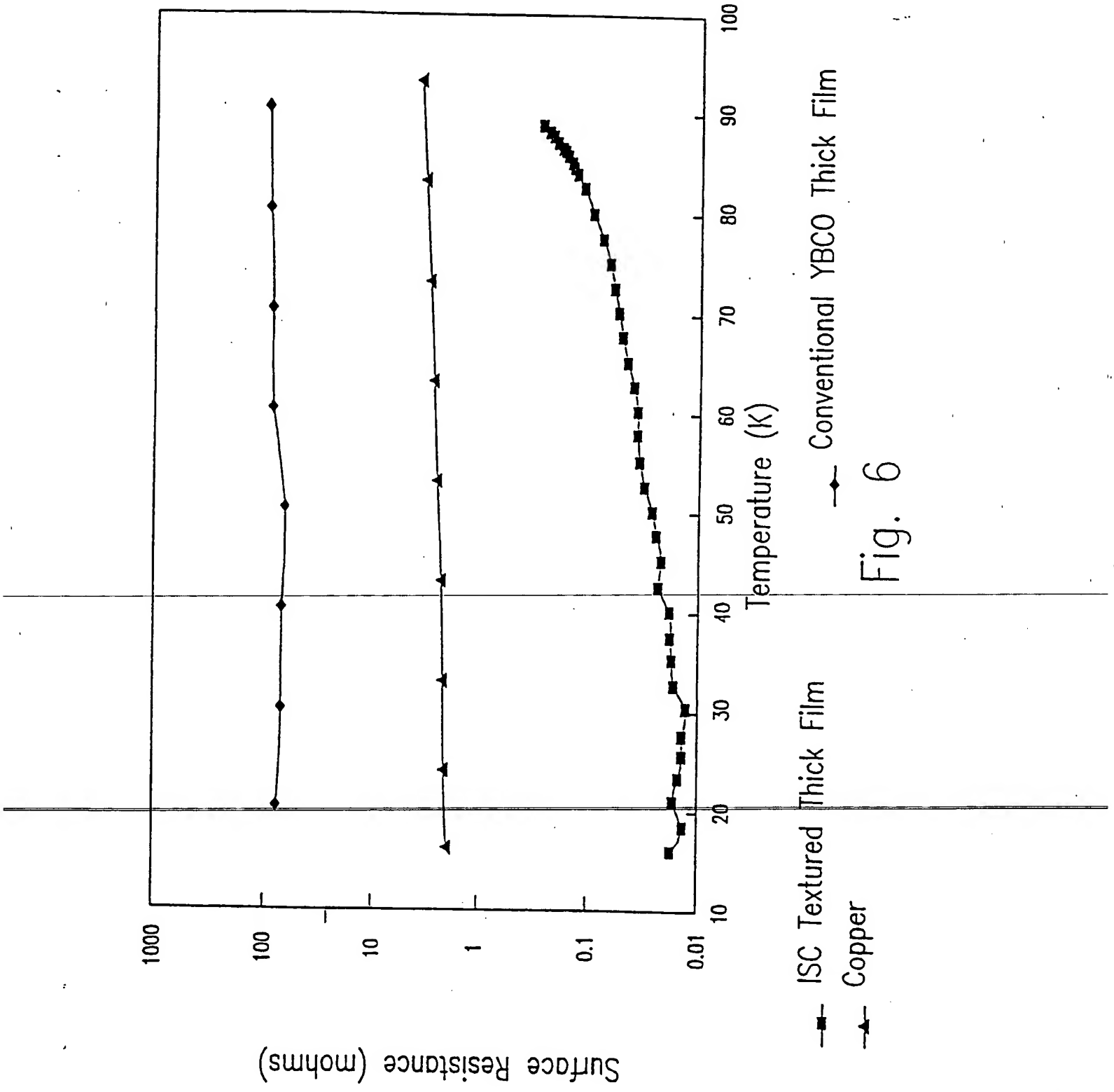

Surface Resistance (mohms)
1000
100
10
1
0.1
0.01
10
20
30
40
50
60
70
80
90
100
Temperature (K)
ISC Textured Thick Film
Copper
Conventional YBCO Thick Film

Fig. 6

Fig. 9A

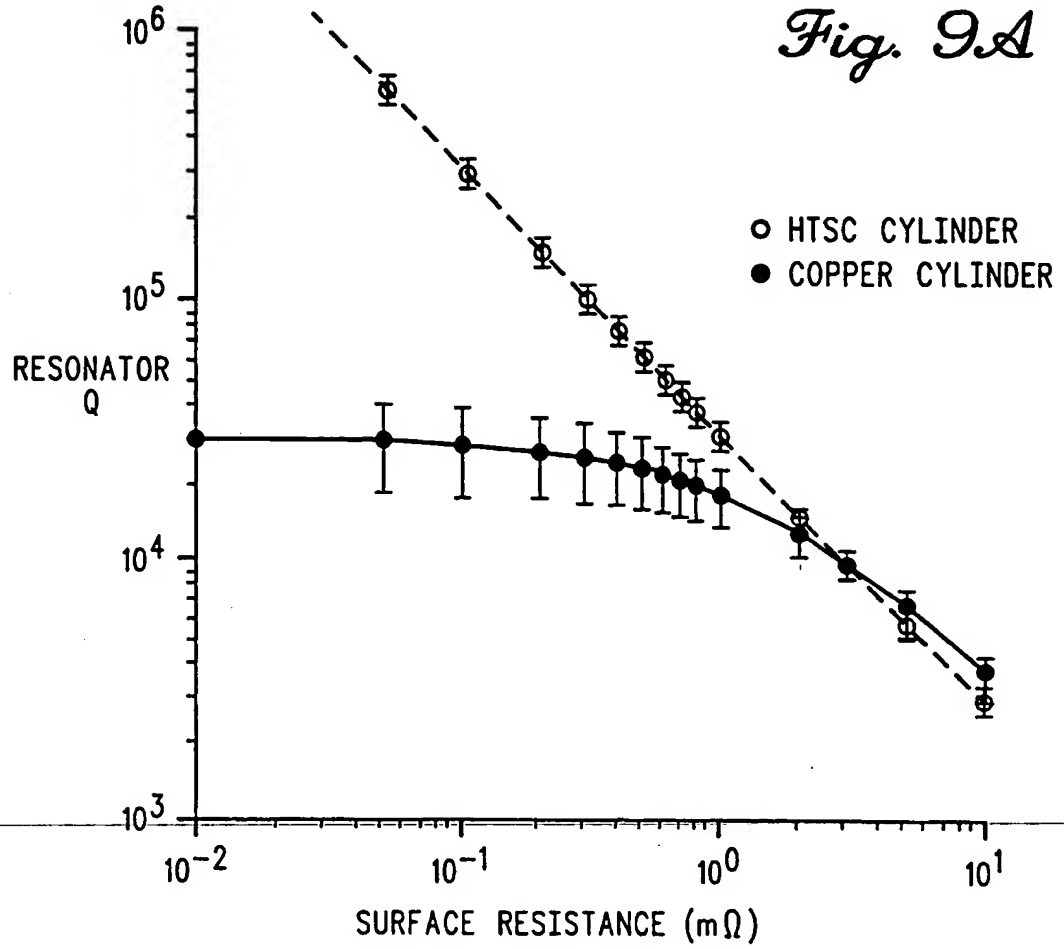
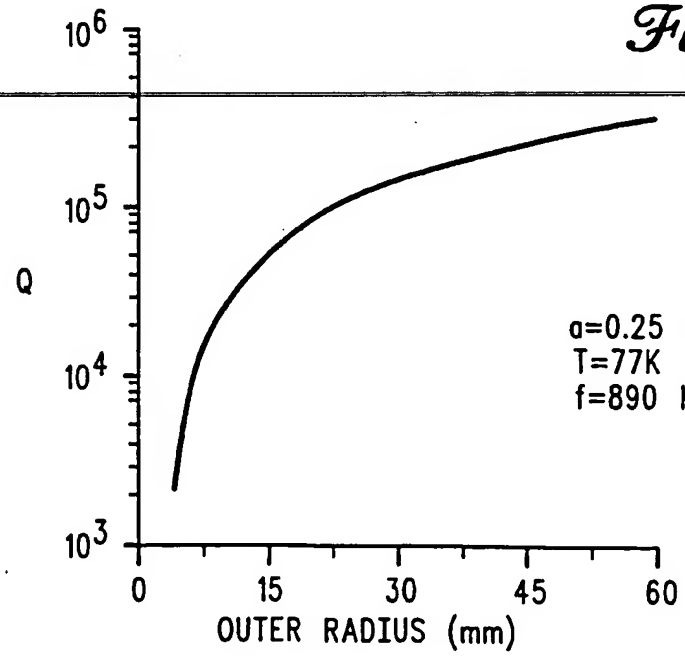

10^6
10^5
10^4
10^3
RESONATOR Q
HTSC CYLINDER
COPPER CYLINDER
10^{-2}
10^{-1}
10^0
10^1
SURFACE RESISTANCE (mΩ)

Fig. 9B


10^6
10^5
10^4
10^3
Q
a=0.25 INCH
T=77K
f=890 MHz
0
15
30
45
60
OUTER RADIUS (mm)

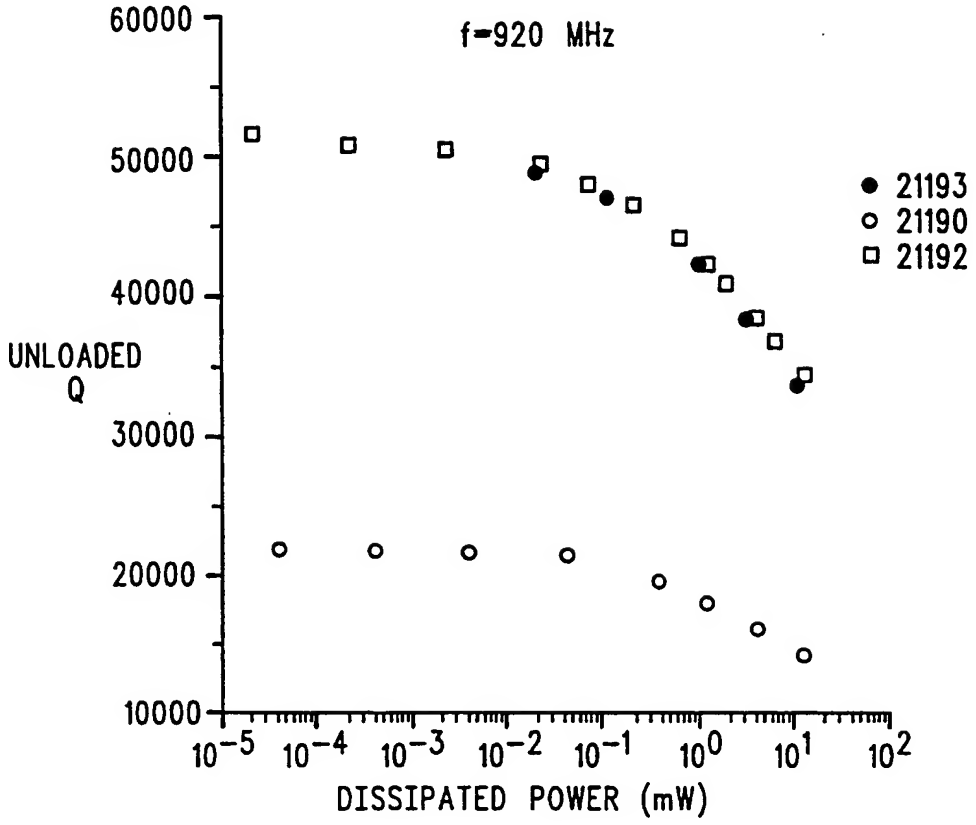

f=920 MHz
60000
50000
40000
30000
20000
10000
UNLOADED Q
21193
21190
21192
10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2}
DISSIPATED POWER (mW)

Fig. 9C

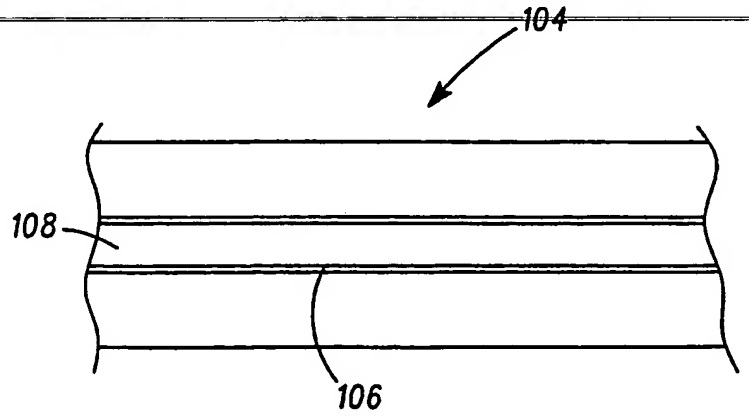

104
108
106

Fig. 10

Fig. 8

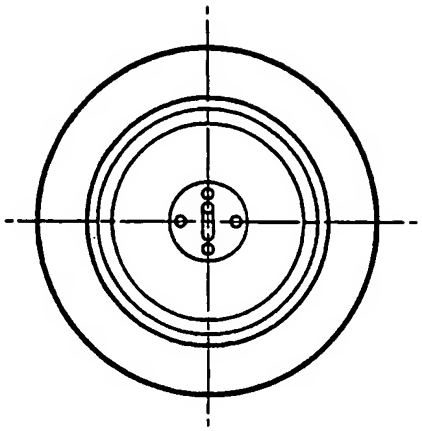


Fig. 7

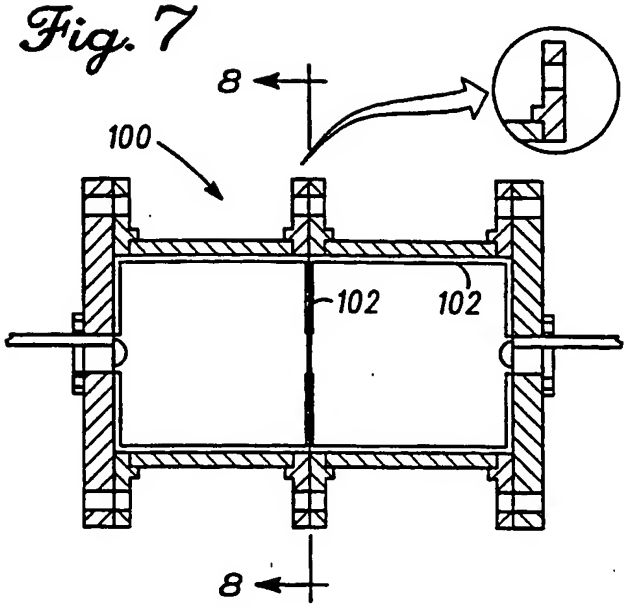
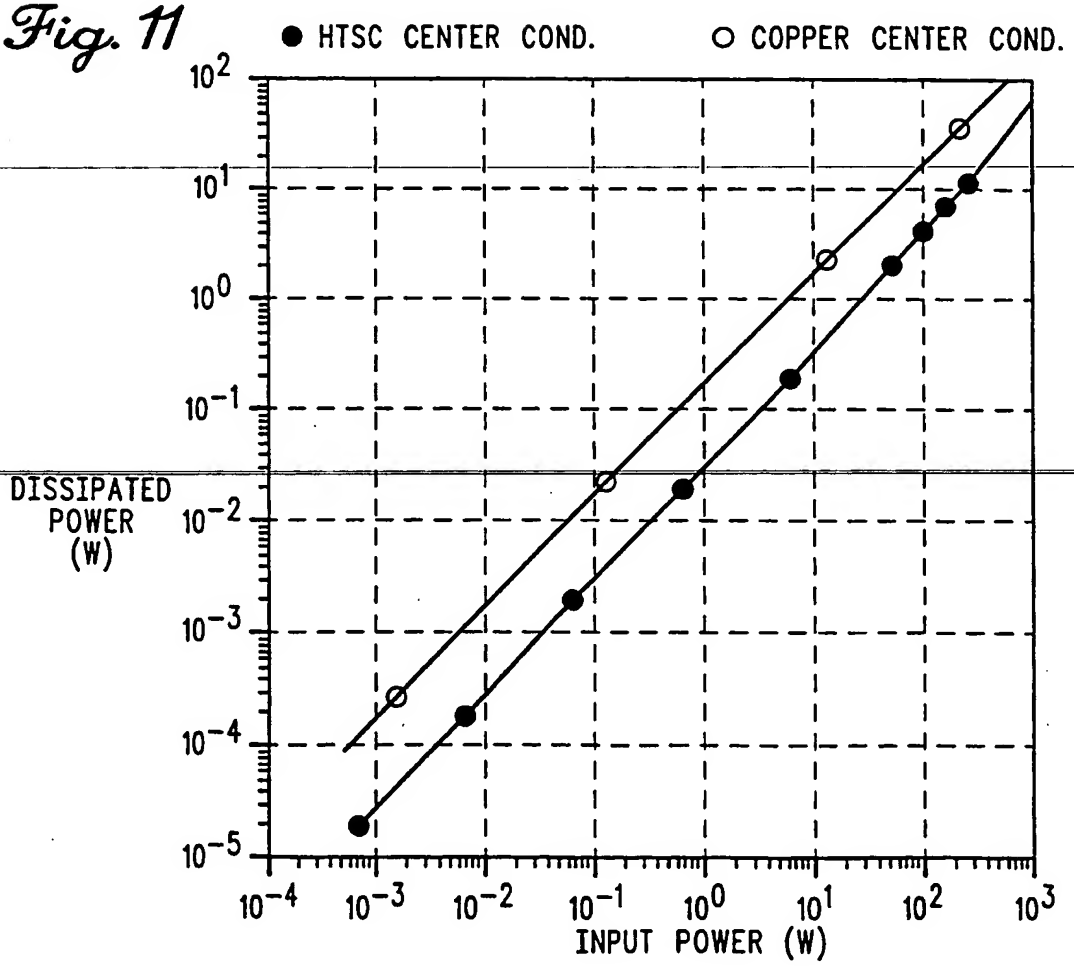


Fig. 11



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12316

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01P 1/208; H01B 12/02; H01L 39/00
US CL :505/210, 236, 700, 701, 866, 126, 450, 500; 333/99S, 212; 427/62; 428/930
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 505/210, 236, 700, 701, 866, 126, 450, 500; 333/99S, 212; 427/62; 428/930, 469. 471; 423/593, 604, 635

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US, A, 5,340,797 (HODGE ET AL) 23 August 1994, see col 3, ls 7-26; col 6, l. 14 - col 8, l. 18.	10,11 -------- 1,3-9
X -- Y	Journal of Material Research, Vol 4, No. 1, January/February 1989, C. T. Cheung et al, "Supercoductor-substrate interactions of the Y-Ba-Cu-O", pages 1-15, see entire document.	10,11 ------- 1,3,5,9
X -- Y	JP, A, 251,903 (KOISHI) 06 October 1989, see abstract & fig. 1.	12,13,15, 20 ---------- 1,3-9,14, 18,19

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 16 OCTOBER 1996	Date of mailing of the international search report 25 OCT 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer BENNY LEE Telephone No. (703) 308 4902

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12316

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X – Y	US, A, 5,407,904 (DAS) 18 April 1995, see fig. 1 & col 3, ls 46-51.	12,13,15, 20 --- 1,3-9,14, 18,19
Y	US, A, 5,106,826 (ALFORD ET AL) 21 April 1992, see fig. 7 & col 7, l. 11 - col 8, l. 43.	2,16,17
A	Popular Science, December 1992 issue, article entitled "Tube within a tube", page 18, note reference to cermic superconductor on a silver tube.	10,11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12316

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-9, 12-14, drawn to a method of manufacturing a superconductive waveguide & a waveguide manufactured by such a method.
Group II, claim(s) 10,11,12,17-19 drawn to a superconductive composite structure & waveguide including such composite structure.
Group III, claim(s) 12,13,15-18,20, drawn to a superconductive cylindrical waveguide.

The inventions listed as Groups I & II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The composite structure of the Group II invention does not require the special technical features (i.e. specific manufacturing steps) as that required in the Group I invention.

The inventions listed as Groups II & III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The superconductive cylindrical waveguide of the Group III invention does not require the special technical features (i.e. composite structure) as that required in the Group II invention.

The inventions listed as Groups I & III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The superconductive cylindrical waveguide of the Group III invention does not require the special technical features (i.e. specific manufacturing steps) as required in the Group I invention.